



CHEMICAL HAZARD SUMMARY

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Methylene Bisphenyl Isocyanate (MDI) and Polymethylene Polyphenyl Isocyanate (PMPPI)

No. 30
ISSN 0827-8830



SCOPE OF THE DOCUMENT

This document focuses on the hazards of methylene bisphenyl isocyanate (MDI) and polymethylene polyphenyl isocyanate (PMPPi). The toxicity, fire and explosion hazards, and reactivity of MDI and PMPPi are described. Information on protective measures, storage, handling, clean-up, disposal, first aid, sampling and analysis is also given. The relevance and perspective of the information for the workplace is emphasized. Special attention is given to the main hazard presented by MDI and PMPPi.

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I. MAIN HAZARD

Both MDI and PMPPI can cause respiratory sensitization. People with this potentially disabling condition can experience severe asthmatic symptoms when they breathe in even very low levels of MDI dust or vapour or PMPPI mist or vapour (see section III. - Effects of Long-Term Overexposure in Humans).

Excessive levels of MDI and PMPPI in the air cause respiratory irritation when inhaled. This condition is different from respiratory sensitization. Very high exposures could prove fatal (see section III. - Effects of Short-Term Overexposure in Humans).

II. OCCUPATIONAL EXPOSURE

At room temperature MDI is a white to light yellow solid with a slightly musty odour. There are several chemical forms of MDI. Commercially available MDI consists mainly of the 4,4' - chemical form. It is used to make Spandex fibres and a few other high-performance rubber-like plastics.

Other modified forms of MDI which are liquid at room temperature are also produced. These are used in reaction injection molding (RIM) systems, in thermoplastic polyurethanes, in elastomer casting systems and in sealants.

PMPPI is also known as "crude" MDI or "polymeric" MDI. At room temperature it is a dark brown, oily liquid with a characteristic earthy, musty smell.

PMPPI is actually a mixture of different isocyanate chemicals. It usually consists of 40-60% MDI (4,4' - form), other MDI forms, and a group of compounds made by joining together parts of MDI chemical units. PMPPI is produced and used in larger amounts than is MDI.

PMPPI is used mainly to make rigid polyurethane foams. It is also used to manufacture no-bake foundry core binders, adhesives, sealants, and coatings such as paints and varnishes.

Material Safety Data Sheets (MSDS) should be available from the manufacturer or supplier of the particular materials. These MSDSs should give details of the isocyanate ingredients contained in the materials. The MSDSs should also give the possible health and safety hazards of the materials and what should be done to control these hazards.

Read and understand the MSDSs and labels for each material before you begin to using it.

No isocyanates are currently produced in Canada. They are all imported for use here.



III. HEALTH HAZARDS

Limitations of the Information on MDI and PMPPI

Each chemical unit of pure MDI has two isocyanate groups. These isocyanate groups cause the harmful effects. It is important to keep in mind that each chemical unit of both PMPPI and modified MDI also has isocyanate groups. This means that these other chemical units, in addition to MDI, could also cause harmful effects to people overexposed to them (21).

Much basic information is lacking on which of the components of PMPPI is most hazardous and the levels of these components which cause health problems. This is because:

1. Most scientific reports state only that "MDI" was studied. This fact is doubtful because PMPPI is much more widely used than MDI. Although MDI is a component, PMPPI also contains a large variable amount of other isocyanate chemicals.
2. Problems in measuring airborne MDI levels have been encountered^(1,2). Measurements of the other components of PMPPI in the workplace have not been reported. This means that *total isocyanate* exposures in workplaces where PMPPI was used may have been underestimated. Similarly, levels of MDI in studies using pure MDI may not be accurate. See Section XI Sampling and Analysis for details.

If PMPPI is specifically mentioned in a study referred to in this hazard summary, it will be indicated.

Routes of Exposure

People can be exposed to MDI and PMPPI in a number of ways:

- i) MDI: Solid – Skin or eye contact, swallowing
Dust – Inhalation, skin or eye contact
Vapour – Inhalation, eye contact
- ii) PMPPI: Liquid – Skin or eye contact, swallowing
Mist (eg. spray mist) – Inhalation, skin or eye contact
Vapour – Inhalation, eye contact

The major risks are associated with breathing PMPPI mist or vapour and MDI dust or vapour.

General information on routes of exposure is available in the CCOHS document "How Workplace Chemicals Enter the Body"⁽³⁾.

Effects of Short-Term Overexposure in Humans

Inhalation

Breathing excessive levels of isocyanate vapours, dusts or mists can irritate the nose, throat and airways of the lungs. Typical symptoms can include a burning feeling in the nose and throat, runny nose, a feeling of chest "tightness",



breathlessness, difficulty in breathing and coughing. Nausea, headache, fever, depression and insomnia might also occur^(4,6).

Breathing very high levels of airborne PMPPI or MDI, which could occur during spraying of these materials or during a large chemical spill or leak, could cause serious effects. Chemical bronchitis, severe asthma-like contractions of the airways of the lungs, and severe coughing spasms may result. Inflammation of the lung tissue (chemical pneumonitis) and fluid in the lungs (pulmonary edema), which could prove fatal, might also develop^(4,5).

Symptoms may not appear until several hours after the exposure^(4,5). The symptoms respond to medical treatment after removal from exposure, although they may persist for several days⁽⁷⁾.

Irritation of the respiratory tract most often happens when airborne isocyanate levels are greater than 0.1 parts of chemical per million parts of air (ppm)^(4,5). People do not usually smell MDI or PMPPI vapours until they reach levels of at least 0.4 ppm. This means that the odour of these chemicals is not a good indicator of possibly hazardous conditions⁽⁵⁾.

Some people develop respiratory sensitization following a single high-level exposure to MDI or PMPPI⁽⁸⁾.

Eyes

PMPPI liquid or MDI dust can irritate the eyes causing watering and discomfort. Vapours of these compounds cause eye irritation. However, the levels needed to cause irritation are much higher than occupational exposure limits⁽⁹⁾. In severe cases of eye contact with liquid or dust, the front part of the eye (cornea) could be damaged⁽⁸⁾.

Skin

Skin contact with liquid isocyanate can cause skin reddening, irritation and dermatitis⁽⁵⁾.

MDI sticks firmly to skin. Irritation may be increased or produced by attempts to remove it from the skin⁽¹⁰⁾.

Ingestion

Swallowing MDI or PMPPI is not a very likely route of workplace exposure. There are no reports of this occurring. The toxicity of these chemicals to animals by this route is low^(7,10). Swallowing large amounts of these compounds might result in irritation and some corrosive action on the mouth, stomach and digestive tract⁽⁸⁾.

Effects of Long-Term Overexposure in Humans

Carcinogenic Effects

There are no reports of either MDI or PMPPI causing cancer in people.



Effects on the Respiratory System

Respiratory sensitization may develop in people who work with PMPPI or MDI. This condition is different from respiratory irritation caused by PMPPI or MDI. Sensitized people can react to very low levels of airborne PMPPI or MDI that would have no effect on unsensitized people. Sensitized individuals can experience symptoms at MDI levels as low as 0.0014 ppm, which is far below current occupational exposure limits⁽¹¹⁾.

At first, the symptoms of respiratory sensitization may appear disguised as a cold or mild hay fever. However, severe asthmatic symptoms can develop⁽⁵⁾. Common effects include difficult breathing, a feeling of chest tightness, coughing (sputum may be present), and fever. Other possible symptoms are shortness of breath, wheezing, general feelings of discomfort, upset stomach, sore throat, shivering, headache, loss of appetite, weight loss, and aching muscles. People experiencing symptoms of respiratory sensitization also have a measurable narrowing of the airways of the lungs^(4,12-19). In some cases, symptoms have been severe enough to require hospitalization^(12,14).

Symptoms can appear immediately after isocyanate exposure, several hours after exposure, or both^(4,13,16). Often, people do not experience symptoms until after they leave work for the day. This can make it difficult to associate effects with exposure to MDI or PMPPI. Symptoms may subside after a few hours if there is no further contact with isocyanates⁽¹⁴⁾. However, some sensitized people have suffered recurrent, night-time asthma attacks for up to seven days after only one exposure to MDI⁽¹⁶⁾.

Sensitized people who continue to work with PMPPI or MDI may develop symptoms sooner and sooner after each exposure. The number and severity of effects may also increase^(13,14,19).

There is little information about what happens to sensitized people who are no longer exposed to PMPPI or MDI. In one case, the breathing problems and lung test results of an MDI-sensitized person showed a progressive improvement during the eight weeks after the end of isocyanate exposure⁽¹⁸⁾. However, another MDI-sensitized person still experienced difficult breathing if he exerted himself. Also, there was no improvement in some of his lung tests after more than a year free of isocyanate exposure⁽¹²⁾.

It is not completely understood how isocyanates cause respiratory sensitization. Responses of the body's immune system may be involved. Up to 20% of the people working in areas where MDI was used have developed respiratory sensitization^(5,20). Both allergy-prone and non-allergy-prone people can become sensitized to PMPPI or MDI^(13,14,16,19). Some people can become sensitized by their first exposure to high levels of airborne MDI or PMPPI⁽⁸⁾. However, most people develop this condition after days, months, or years of working with these materials⁽¹²⁻¹⁵⁾. In general, people who have been exposed to very high levels of airborne isocyanates seem to be more likely to develop respiratory sensitization to isocyanates^(4,15).



It is not possible to say what level of PMPPI or MDI exposure will cause someone to develop respiratory sensitization. Generally, it seems that the lower the concentration of airborne isocyanates, the smaller the number of people who become sensitized.

It is also not clear whether pure MDI is more likely to cause respiratory sensitization than PMPPI.

Cross-sensitization between different isocyanate chemicals can occur. This means that people sensitized to one isocyanate chemical can suffer similar symptoms when they inhale a different isocyanate chemical to which they have never been exposed. People sensitized to TDI (toluene diisocyanate) have shown sensitization to both MDI and HDI (hexamethylene diisocyanate) without previous exposure to these two chemicals⁽¹¹⁾. A person sensitized to HDI-containing enamel also showed symptoms of respiratory sensitization to PMPPI. There had been no previous exposure to PMPPI⁽¹⁷⁾.

Breathing MDI and PMPPI for years may cause other respiratory system problems besides respiratory sensitization. Two studies indicate that a progressive, greater- than-normal decrease in lung capacity, as measured by lung tests, might occur in people exposed to airborne MDI for years. The decrease was greatest in people with long exposure times. Those who were thought to be exposed to higher levels of MDI had more respiratory symptoms. They also had a greater decrease in lung capacity. Detailed information on the airborne MDI levels to which they were exposed was not provided⁽²¹⁾.

People exposed for up to ten years to combined MDI and TDI levels averaging around 0.003 ppm did not have abnormal decreases in lung capacity⁽²¹⁻²³⁾. Problems can arise in this type of study because of difficulties in getting accurate information on worker exposures to isocyanates⁽⁴⁾.

Effects on the Skin

Repeated skin contact with both MDI and PMPPI can cause skin sensitization. People with this condition show symptoms of dermatitis such as skin inflammation, rash and itching whenever they touch these materials with unprotected skin^(9,24).

MDI compounds have a mild tanning action on the skin⁽⁹⁾. Foundry workers using oil-base no-bake binding systems containing MDI can develop dark stains on their unprotected hands. These stains cannot be removed by normal hand cleaning methods although they do gradually wear off if there is no more skin contact with the material⁽²⁵⁾.

Toxicity Data in Animals and Laboratory Tests

Lethal Dose Values

The poisoning strength of a compound can be estimated from the LD₅₀ or LC₅₀ obtained in animal tests. LD stands for lethal dose, LC for lethal concentration in air. The LD₅₀ is the amount of a chemical (weight of chemical per weight of animal) which is needed to kill 50% of the test animals. The LC₅₀ is the concentration in air which kills 50% of the animals following an exposure lasting



4 hours or another indicated time period. Test animals are usually rats, mice or other rodents. Routes of exposure are usually by mouth (oral), through the skin (dermal) or by breathing in the airborne chemical (inhalation). The values obtained for these materials by different researchers are:

	PMPPI	MDI
LD ₅₀ (rat, oral)	Greater than 10 000 mg/kg* body weight	31 600 mg/kg body weight
LD ₅₀ (rabbit, dermal)	Greater than 5 ml/kg** body weight	Greater than 10 000 mg/kg body weight
LC ₅₀ (rat, inhalation)	No data	369-490 mg/m ³ ***/ 4 hr; 178 mg/m ³ - exposure duration unknown; greater than 400 mg/m ³ /2 hr

*Milligrams of chemical per one kilogram of the test animal's body weight.

**Millilitres of chemical per one kilogram of the test animal's body weight.

***Milligrams of chemical in one cubic metre of air.

These results indicate that:

1. MDI is very toxic when it is breathed in.
2. MDI and PMPPI are not very toxic when they are applied to the skin.
3. MDI and PMPPI are not very toxic when they are swallowed.

Further general information on the LD₅₀ is available in the Centre's publication "What is an LD₅₀?"⁽²⁶⁾.

Other Animal Data

No harmful effects were seen in rats inhaling PMPPI vapour at 0.2 ppm for 8 hours. Harmful effects were not observed when rats breathed 0.2, 0.65, or 2.6 ppm of PMPPI for 30 minutes a day, 5 days a week for 2 weeks⁽⁵⁾.

Guinea pigs inhaling 4.6 mg/m³ of PMPPI or 0.94 mg/m³ of MDI for 4 hours a day, for 5 days developed symptoms resembling respiratory sensitization when re-exposed to airborne PMPPI and MDI⁽²¹⁾. In all of these cases, the levels of airborne isocyanate used was very high. Such high exposures are not likely under normal conditions in most industrial workplaces using these chemicals.

Dogs which had MDI placed into the airways of their lungs developed both skin and respiratory sensitization to MDI. PMPPI has caused a skin sensitization reaction when applied to the skin of guinea pigs that had previously inhaled MDI⁽²¹⁾. Such effects have not been seen in people exposed to these materials.



MDI can easily cause skin sensitization in guinea pigs. It can also cause an allergic skin response in animals with skin sensitization to TDI⁽²⁷⁾.

Pure MDI applied to rabbit skin causes mild irritation that usually clears after several days^(5,27). A commercial brand of PMPPi applied for 24 hours to intact or scraped rabbit skin under a bandage produced only minor skin changes⁽⁵⁾. MDI or PMPPi are slightly irritating when applied to rabbit eyes^(5,27).

A genetic mutation is a change in the genetic material located in the chromosomes of body cells. Genetic mutations may lead to birth defects or cancer. MDI did not cause chromosome damage in mice (micronucleus test)⁽²¹⁾. MDI caused genetic mutations in two of three short-term tests using bacteria (Ames test)^(5,28). PMPPi caused genetic mutations in one short-term Ames test⁽²⁸⁾. The significance of these results for people exposed to MDI or PMPPi is not known.

In test-tube experiments MDI, affects an enzyme involved in nerve impulse transmission. This may explain some respiratory effects caused by MDI⁽²¹⁾.

IV. FIRE AND EXPLOSION HAZARDS

PMPPi and MDI are not flammable under normal conditions. However, in the presence of an existing fire or other situation where they can be heated enough, they will burn. Toxic carbon monoxide, oxides of nitrogen and some hydrogen cyanide may be given off.

The fire hazard can be estimated by the flash point of the substance. The flash points of MDI, PMPPi and modified MDI products are typically greater than 149°C (300°F). When the material is at or above this temperature, enough vapour is produced to form a flammable or explosive mixture of vapour and air. A spark, flame or other ignition source can cause this mixture to burn or explode.

Fire Extinguishing Agents

Large fires involving isocyanates can be extinguished with water spray. Use large quantities of water since the reaction between water and hot isocyanate can be vigorous.

High expansion chemical foam, carbon dioxide or dry chemical extinguishers can be used for smaller fires⁽⁸⁾.

V. CHEMICAL REACTIVITY

At temperatures below 50°C (122°F) MDI and PMPPi react very slowly with water to form carbon dioxide gas and relatively harmless, unreactive solids. At higher temperatures, the reaction becomes progressively more vigorous and can be violent.



PMPPI and MDI may react violently with amines, bases, alcohols and acids. The reaction may generate heat which can result in an increased amount of isocyanate vapour and the formation of carbon dioxide. This can lead to a build-up of pressure and possible rupture of closed containers. Do not reseal isocyanate containers if you suspect contamination of the material inside them.

MDI does not generally corrode metals at normal temperatures. PMPPI is slightly acidic and may produce some corrosion to copper alloys and aluminum.

Isocyanates may attack and cause brittleness in many plastic and rubber materials in a short time⁽⁹⁾.

VI. EXPOSURE LIMITS

Many Canadian jurisdictions have exposure limits similar to those established by the American Conference of Governmental Industrial Hygienists (ACGIH). The exposure limit recommended by ACGIH for MDI is a time-weighted average value of 0.005 parts per million (ppm) or 0.055 milligrams per cubic metre (mg/m³)⁽²⁹⁾. Refer to ACGIH documentation for information on the exposure limits.

An exposure limit for PMPPI has not been set.

Contact the appropriate authority in your jurisdiction for details of the specific regulations which apply. British Columbia and Ontario have special isocyanate regulations.

VII. EXPOSURE CONTROLS

Exposure to MDI or PMPPI is best prevented by design of the work process and engineering controls. The available types of control measures include:

Substitution	Area ventilation
Isolation	Work practices
Enclosure	Personal hygiene
Local exhaust ventilation	Personal protective equipment

One or more of these measures may be appropriate in any particular situation. A survey of the workplace and consideration of the technical requirements of the work process are usually needed before major changes are made. Regular worker training should ensure that all employees have current knowledge of job hazards and procedures, including emergency procedures.

Use fully-enclosed handling systems where possible. Local exhaust ventilation may be necessary in operations such as weighing, dispensing and mixing of isocyanate-containing materials. Spraying operations, and moulding and curing of foams or rubbers may also require local exhaust ventilation. Supply enough clean air to the work area to replace air removed by exhaust ventilation systems.



Design and maintain all control systems to keep isocyanate exposures as low as possible.

Preferred methods of control are substitution of MDI or PMPPI with a less toxic material (if possible) and engineering changes. Personal protective equipment increases the level of protection for workers exposed to this material. In some situations, such as working in confined spaces and in some maintenance operations, the use of personal protective equipment may be essential since effective ventilation and engineering controls might not be possible.

Protective Clothing

Wear protective clothing (gloves, coveralls, boots, etc.) as needed to prevent skin contact with MDI or PMPPI. Clothing made with polyvinyl alcohol (PVA) or polyvinyl chloride (PVC) may provide resistance to penetration and clothing destruction by either MDI or PMPPI^(9,30,31). Clothing made with natural rubber may also be suitable for working with PMPPI⁽³⁰⁾. Clothing made from butyl rubber or nitrile rubber may be resistant to MDI⁽³¹⁾. Evaluate the effectiveness of protective clothing under actual conditions of use and maintain it carefully.

Promptly remove clothing which becomes contaminated with isocyanates and place in a closed container. Discard or decontaminate and launder before re-wearing. Decontaminate clothing by putting it in a solution of 3-8 parts by volume concentrated ammonia solution, 2 parts by volume detergent and 90-95 parts by volume water before laundering⁽⁸⁾.

Wear chemical safety goggles to protect the eyes when working with isocyanates. A face shield may also be necessary to protect the face.

Wear protective coveralls, gloves, footwear and suitable respiratory protection when working close to inadequately ventilated spray operations, or wherever there is a drift of spray⁽⁶⁾. A safety shower and eye-wash station should be readily available wherever MDI or PMPPI are present.

Respiratory Protection

Factors to be considered when implementing a respiratory protection program include:

- Selection of appropriate respirators
- Respirator fit
- Respirator maintenance
- Worker training

These factors are described in more detail in CSA Standard Z94.4 "Selection, Care, and Use of Respirators", available from the Canadian Standards Association, Rexdale, Ontario, M9W 1R3.

NIOSH⁽³²⁾ recommends the following respiratory protection for MDI concentrations of:



0.2 ppm (2.0 mg/m³) or less:

Any supplied-air respirator (SAR)*; or any self-contained breathing apparatus (SCBA)*.

0.5 ppm (5.0 mg/m³) or less:

Any SAR operated in a continuous-flow mode*.

1 ppm (10 mg/m³) or less:

Any SCBA with a full facepiece; or any SAR with a full facepiece.

10 ppm (100 mg/m³) or less:

Any SCBA with a full facepiece and operated in a pressure-demand or other positive pressure mode.

Emergency or planned entry in unknown concentration or conditions immediately dangerous to life or health (IDLH)**:

Any SCBA with full facepiece and operated in a pressure-demand or other positive-pressure mode; or any SAR with a full facepiece and operated in pressure-demand or other positive-pressure mode in combination with an auxiliary SCBA operated in pressure-demand or other positive-pressure mode.

Escape:

Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapour canister having a high-efficiency particulate filter; or any appropriate escape-type SCBA.

* Substance reported to cause eye irritation or damage. Eye protection may be required.

** For purposes of respiratory protection, IDLH is defined as the highest concentration of a substance from which a person could escape within 30 minutes and not suffer symptoms that would impair escape, or any irreversible health effects. For airborne MDI, the IDLH concentration is 10 ppm (100 mg/m³).

Note: The above recommendations apply only to equipment approved by NIOSH/MSHA.

VIII. SMALL-SCALE STORAGE AND HANDLING

Store MDI and PMPPI in tightly-closed, labelled containers. Keep containers in a dry, well-ventilated area, out of direct sunlight. Store them away from materials that react chemically with MDI and PMPPI. Keep containers away from heat and ignition sources and protect them from damage. Store at manufacturer's recommended temperatures. Store MDI and PMPPI in quantities as small as possible.



Storage areas should have floors that do not allow spilled liquids to penetrate. Storage areas should also be diked to contain spills. Consider installing leak detection and alarm equipment. Only allow authorized trained persons access to the storage area. Separate chemical storage areas from populated work areas. Post appropriate warning signs. Inspect storage areas regularly for any defects such as leaking containers.

Very carefully melt pure MDI according to manufacturer's recommendations⁽⁹⁾.

Use MDI and PMPPI in the least possible quantities in designated well-ventilated areas. Do not use near sources of heat or sparks. Use labelled containers and keep them closed when not in use. Protect containers from damage. Do not reseal containers if contamination of the isocyanate inside is suspected. Avoid handling MDI and PMPPI in open vessels as much as possible. Wear protective goggles, clothing and respirator suitable for the job being done. Empty MDI and PMPPI containers may be hazardous due to material remaining inside them. Decontaminate empty drums by filling them with *one* of the following solutions*:

- i) 3-8 by volume concentrated ammonia solution, 2 parts by volume detergent, 90-95 parts by volume water
- ii) 20 parts by volume non-ionic surfactant (such as Union Carbide TMN-10*), 80 parts by volume water⁽⁸⁾
- iii) 5% sodium carbonate, 95% water⁽⁹⁾

Allow the drums containing decontaminating solution to stand uncovered outdoors or in a safe, well-ventilated area for at least 24 hours^(8,9). The reaction between the solution and isocyanate liberates carbon dioxide gas that could rupture tightly-closed containers.

Decontaminate (using above solutions i or ii) and clean isocyanate handling equipment after use.

Dispose of decontaminant solutions according to local environmental regulations.

In general, MDI and PMPPI should be stored and handled in ways which minimize the risks of spillage and the release of vapour or particles into the workplace air.

*This product name is only used as an example. Mention of it in this document does not constitute an endorsement of its use or effectiveness by the Canadian Centre for Occupational Health and Safety.

IX. CLEAN-UP AND DISPOSAL

MDI and PMPPI are potentially very hazardous materials. Exposures associated with isocyanate spills can be high and could cause serious health problems. A plan should be established to deal with emergencies such as spills or leaks.



Trained crews should be available to handle emergencies. The chemical supplier or manufacturer can provide advice on how to deal with emergency situations.

Minor spills are spills that can be handled by the people and equipment available at the workplace. A major spill is one that requires help from outside sources such as the supplier/manufacturer, police or fire services. For emergency situations while transporting MDI or PMPPI, call the Canadian Transport Emergency Centre (CANUTEC). Call CANUTEC collect at (613) 996-6666, 24 hours a day, seven days a week, including holidays.

The following general actions can be useful in case of a spill of MDI or PMPPI: Evacuate the spill area. Provide assistance to injured or contaminated persons. Do not allow unauthorized people into the area of the spill until clean-up operations are finished. Wear personal protective equipment, including a proper respirator, to minimize exposure to isocyanates. Notify government occupational health and safety and environmental agencies.

Eliminate all ignition sources and ventilate the spill area. Do not touch the spilled material. Stop or reduce the rate of leaking if it can be done safely. Move leaking containers outdoors or to an isolated well-ventilated area and transfer the contents to a clean, undamaged container if it can be done safely. Prevent material from spreading or entering sewers or confined spaces by diking with earth, sand or commercially available non-reactive sorbent materials. MDI or PMPPI will react with water to form solid residues that could cause blockage of drains.

Use decontaminant solution (i or ii in Storage and Handling) to decontaminate spilled material. The total weight of decontaminant solution used should be greater than the weight of spilled MDI or PMPPI. Heat and carbon dioxide gas result when isocyanates react with the solution. Use clean, undamaged, labelled, open containers to hold clean-up residues.

Minor spills of PMPPI or modified MDI (liquid): Cover spill with sand, earth or non-reactive absorbent material. Slowly, with stirring, pour decontaminant solution onto the spill. Allow to react for 10 minutes. Shovel all residues into open containers. Remove them to a safe, well-ventilated area.

Minor spills of MDI (solid): Shovel into open containers. Move to safe area for disposal. Wash down spill area with decontaminant solution. Allow to react for at least 10 minutes. MDI is often shipped and stored in a liquid (melted) state. To clean up these spills, allow the melted material to solidify then clean up as solid MDI⁽³¹⁾.

Major spills of MDI, PMPPI or modified MDI: Contact local police, fire services and the isocyanate supplier for assistance, especially if on-site decontamination is impractical.

In all cases, carefully add extra decontaminant solution to each open container holding spill residues to ensure all isocyanate has reacted. Store open or loosely covered containers at least 24 hours before disposal. Wash down the spill area with large amounts of water or decontaminant solution. Decontaminate



emergency equipment. Test the air for isocyanate levels. When safe working conditions have been established, resume normal operations^(9,31).

Solidified spills: Remove these by abrasive blasting or treatment with a chlorinated solvent followed by normal decontamination. Use protective clothing and respirators to protect the people involved⁽⁹⁾.

Consult local environmental authorities before disposal of material containing isocyanates.

X. FIRST AID

The following general procedures are suggested for first aid involving poisoning by MDI or PMPPI:

Inhalation

Take proper precautions to ensure your own safety before attempting rescue, for example wear appropriate protective equipment, use the "buddy" system. Remove source of contamination or move victim to fresh air. Obtain medical attention immediately.

Skin

Avoid direct contact with this chemical. Wear impervious protective gloves and respiratory protection if necessary. Remove contaminated clothing, shoes and leather goods (for example watchbands, belts) and place in covered container. As quickly as possible, flush contaminated area with lukewarm, gently running water for at least 20 minutes, by the clock. If irritation persists, wash gently and thoroughly with water and non-abrasive soap. Obtain medical attention immediately.

Eyes

Gently blot or brush away excess chemical quickly. Immediately flush the contaminated eye(s) with lukewarm, gently flowing water for 20 minutes, by the clock, holding the eyelid(s) open. Obtain medical attention immediately.

Ingestion

Never give anything by mouth if victim is rapidly losing consciousness or is unconscious or convulsing. Rinse mouth thoroughly with water. **DO NOT INDUCE VOMITING.** Have victim drink about 250 ml (8 ounces) of water to dilute material in stomach. If vomiting occurs naturally, have victim lean forward to reduce risk of isocyanates entering the lungs. Repeat administration of water. Obtain medical attention immediately.

Note: Consult a physician and/or the nearest Poison Control Centre for all cases of ingestion or eye contact and all but trivial cases of inhalation or skin contact.

All first aid procedures should be periodically reviewed by a physician familiar with MDI and PMPPI and their conditions of use in the workplace.



XI. SAMPLING AND ANALYSIS

Various sampling and analysis methods are available to determine airborne MDI levels^(1,2,6). Methods have been developed that might be used to measure modified MDI or airborne PMPPi⁽³³⁻³⁵⁾.

Problems in measuring airborne MDI levels have been reported. An important reason for this is that, depending on conditions, MDI can be in the air as a vapour or an aerosol, or both. This can affect the choice of sampling method used. Occupational exposures to MDI less than 0.005 ppm may be mostly to MDI vapour so that impinger techniques could be used for sampling. Airborne MDI vapours start to condense and form aerosols at MDI levels above 0.005 ppm at normal room temperature (25 deg C)⁽¹⁾. As a result, levels of MDI greater than 0.005 ppm may be underestimated by impinger methods.

MDI sampling methods using filters seem to collect MDI better than impinger methods regardless of airborne MDI level or whether MDI is a vapour or aerosol⁽¹⁾.

Direct reading instruments are available which respond to airborne MDI. Care should be taken in interpreting the readings from such instruments where exposure to isocyanate aerosols or mixed isocyanates occurs⁽³⁶⁾. Some instruments are more sensitive to MDI than others⁽¹⁾.

Problems have been encountered with some methods that might be used to measure modified MDI or PMPPi. NIOSH intends to discontinue Method 5505⁽³⁵⁾. No information is available on the ability of direct reading instruments to accurately measure airborne modified MDI or PMPPi levels.



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Note: Additional references on this subject are available from CCOHS upon request.

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The information in this document was updated on January 8, 1987.

Cat. No. CC273-4/87-10E
ISBN 0-660-12628-1
CCOHS C87-10E